Influence of active phase loading in hydrodeoxygenation (HDO) of ethylene glycol over promoted MoS2/MgAl2O4 catalysts

Dabros, Trine M. H.; Kramer, Hendrik ; Høj, Martin; Grunwaldt, Jan-Dierk ; Gabrielsend, Jostein ; Jensen, Anker Degn

Publication date:
2018

Document Version
Peer reviewed version

Influence of active phase loading in hydrodeoxygenation (HDO) of ethylene glycol over promoted $MoS_2/MgAl_2O_4$ catalysts

Trine M. H. Dabros[1,2], Hendrik Kramer[1,3], Martin Høj[1], Jan-Dierk Grunwaldt[4], Jostein Gabrielsen[2], Anker Degn Jensen[1]*.

1 – Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, 2800, Denmark.
2 – Haldor Topsøe A/S, Kgs. Lyngby, 2800, Denmark.
3 – IWT Foundation Institute of Material Science, University of Bremen, Bremen, 28359, Germany.
4 –Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, 76131, Germany.
** aj@kt.dtu.dk*

1. Introduction

Catalytic fast hydropyrolysis can be used to convert solid lignocellulosic biomass into liquid fuels by combined fast pyrolysis and catalytic hydrodeoxygenation (HDO) [1]. The advantage of this technique is that the pyrolysis vapors can be deoxygenated and stabilized against polymerization immediately when formed, since fast pyrolysis occurs in the presence of an HDO catalyst and hydrogen. Promoted MoS_2 catalysts are active and selective for HDO [2]. Since the cellulosic part of biomass contributes to polymerization and coking [3], a key focus of the catalyst and process development is to investigate HDO of cellulose and hemicellulose derived compounds. Ethylene glycol (EG) represents these compounds and was used as model compound in this work.

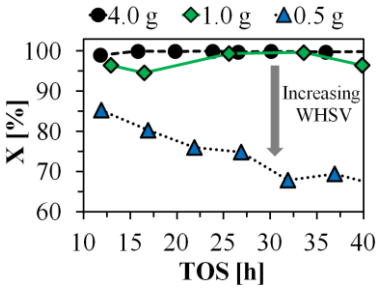

Figure 1. EG conversion (X) versus time on stream (TOS) over moderate loading Ni-$MoS_2/MgAl_2O_4$ for different EG WHSV (2, 9, and 18 h^{-1}).

2. Experimental

Catalysts (Ni- and Co-promoted $MoS_2/MgAl_2O_4$) where prepared at different active phase loading by incipient wetness impregnation followed by *in-situ* sulfidation in a fixed bed reactor setup, which was also used for activity testing. In activity tests, 0.5-4.0 g catalyst was loaded into the reactor, and ethylene glycol was fed at ≈ 0.15 mL/min giving a weight hourly space velocity (WHSV) of 2-19 $g_{EG}/(g_{cat}\cdot h)$. Activity tests were run for up to 172 h at 400 °C, a total pressure of 40 barg, 27 bar H_2, and a co-feed of H_2S typically around 550 ppm. Gaseous products were quantified with GC-TCD, while liquid products and unconverted EG were quantified with GC-MS/FID. Fresh and spent catalysts were analyzed with BET, TEM, ICP-OES, XRD, and Raman spectroscopy.

3. Results and discussion

The conversion of EG over the pure $MgAl_2O_4$ support (WHSV = 9 h^{-1}) showed that it catalyzed coupling reactions such as alcohol condensation, dehydration, and acetalization. The conversion of EG over low (L, 0.8-0.9 wt% Mo) and moderate (M, 2.8-3.4 wt% Mo) loading catalysts showed that Ni- and Co-MoS_2 catalyzed both HDO (giving ethane and ethylene (C_2)) and cracking (giving CO, CO_2, and CH_4 (C_1)). There was a higher selectivity towards HDO as seen from the C_2/C_1 yield ratio of 1.1-1.5, independent of catalyst loading (see Table 1). The moderate loading catalysts showed superior hydrogenation activity (ethane formed rather than ethylene), whereas the low loading catalysts formed a mixture of ethylene and ethane during activity tests (see Table 1). The EG conversion was > 90 % for all catalysts at an EG WHSV of 2 h^{-1}. Catalyst deactivation was observed for the low loading catalysts (WHSV = 2 h^{-1}), and by increasing the WHSV, deactivation could also be observed for the moderate loading catalysts (see Figure 1). Carbon deposition was the main reason for catalyst deactivation, determined by TEM, elemental analysis and Raman spectroscopy.

4. Conclusions

Ni-MoS_2 and Co-MoS_2 supported on $MgAl_2O_4$ is active and selective for HDO. The MoS_2 based active phase catalyzes HDO, but also cracking, with a C_2/C_1 yield ratio >1. The active phase loading and WHSV influences the hydrogenation activity and the level of deactivation.

Table 1. EG conversion (X) and selected carbon based yields (Y). WHSV = 2 h^{-1} (for $MgAl_2O_4$, WHSV = 9 h^{-1}). TOS = 14-20 h. ETA: ethane. ETY: ethylene.

Catalyst	Loading [wt%]	X [%]	Y_{ETA} [%]	Y_{ETY} [%]	Y_{C2}/Y_{C1}
(L) Ni-MoS_2	Mo:0.83 Ni: 0.17	99	3.4	7.5	1.2
(L) Co-MoS_2	Mo: 0.88 Co: 0.16	96	2.5	8.2	1.3
(M) Ni-MoS_2	Mo: 2.83 Ni: 0.58	100	43	0	1.4
(M) Co-MoS_2	Mo: 3.28 Co: 0.59	100	44	0	1.4
$MgAl_2O_4$	-	25	0.2	0.9	1.6

References

[1] L.P. Resende, *Catal. Today* **269** (2016) 148.
[2] T.M.H. Dabros, A. Gaur, D.G. Pintos, P. Sprenger, et al., Appl. Catal. A 551 (2018) 106.
[3] W. Yin, A. Kloekhorst, R.H. Venderbosch, et al., *Catal. Sci. Technol.* **6** (2016) 5899.